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Mechanisms of photoluminescent quenching of oxidized porous silicon
Applications to chemical sensing

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Contents

Abstract

Silicon can be caused to photoluminesce in the visible by rapid anisotropic etching of bulk samples to form a porous material. Both electrochemical and chemical etching procedures based on an HF reagent have been developed for this purpose. Porous silicon is found to contain nanoscopic silicon particles which have been identified as the luminescent species. The observed photoluminescence is very sensitive to the surface preparation of the porous silicon. Light oxidation of the porous silicon substrate produces a material which is selectively sensitive to Brönsted bases, sulfur dioxide, and halogens. Selective quenching of oxidized porous silicon is associated with the presence of specific types of dangling bond surface states (P_{b0} and P_{b1}) at the silicon/silicon oxide interface. Interfaces of this type can be fashioned into environmental sensors. Using this approach a gas phase sulfur dioxide sensor has been demonstrated. © 1998 Elsevier Science S.A.

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1. Introduction

The recent surge in research related to porous silicon (PS) stems largely from the belief that the efficient visible photoluminescence (PL) observed at room temperature [1] can be translated into electroluminescence from the same material. Electroluminescence from silicon is highly desirable, with obvious application to optoelectronic and display technologies. During this recent flurry of research activity, many other interesting effects related to the chemistry of porous silicon have been discovered. These findings have led to an expanded knowledge of porous silicon photophysics and a greater number of applications in new fields, particularly in the area of sensors.

2. Generation of porous silicon

Formation of PS is performed using one of two general types of reaction. An electrochemical procedure can be used to anodize silicon in an HF solution. The porous silicon formation occurs where the holes emerge from the wafer. Alternatively, a chemical approach may be taken, in which an etching solution containing HF and an oxidizing agent is employed. The silicon needs only to be exposed to the solution to etch it and no applied bias is required. We have previously demonstrated a modification on the stain etchant which provides an excellent yield of porous silicon [2]. In this system sodium nitrite is added to the classic stain etch as a NO^+ generator. This species provides the necessary oxidizing equivalents.

The electrochemical etch provides greater control over etching parameters while etching is in progress. Current density, for example, has an effect on the color of light emission from the porous silicon product. Increasing the current density results in a more porous final product and blue shifts the emission maximum [3]. By increasing current density it is possible to create a porous layer whose emission appears green rather than the usual red–orange. The porosity of the final product is also influenced by other factors such as hydrofluoric acid concentration. Increasing HF concentration of the electrochemical etching solution results in a less porous final product [3].

Porous silicon layers generated utilizing chemical etches cannot be grown as thick as electrochemical layers, but chemical etching offers certain advantages over electrochemical etching. Large pieces of silicon or silicon powders cannot be conveniently anodized, but chemical etches can yield strongly luminescent samples on any silicon that can be immersed in the etchant. Chemical etches are dependent upon injecting holes into the silicon from the front side, unlike electrochemical etches, so by masking parts of the silicon it is possible to generate patterns of luminescent porous silicon and non-luminescent silicon on a wafer.

Chemical etches are also interesting in what they reveal about the luminescence mechanism. Initially, it was assumed that porous silicon emitted through either a simple band to band like transition in a quantum confined system, or by a surface bound molecular luminophore. The actual luminescence mechanism has proven to be far more complex than either of these models [4]. The photoluminescence emission spectra obtained for chemical etches are quite similar to one another, having λ_{max} near 625 nm. However, the excitation profile is quite dependent upon the concentration of strong acid employed. Without altering the HF concentration or the amount of $NaNO_2$ (oxidizing agent), the excitation maxima can be shifted from ~220 nm to ~300 nm by changing from a 1:1 H_2O/H_2SO_4 solvent to concentrated H_2SO_4 [2]. Clearly, a lower energy photon is required to produce photoemission from porous silicon generated in more acidic etchants, but the light emitted is of the same energy. This observation is not easily explained by either model, and is indicative of the complexity of the problem.

3. Quenching mechanisms

Sailor and coworkers [5–7], Coffer et al. [8,9], Anderson et al. [10,11], McLendon and coworkers [12,13], Meyer and coworker [14,15], and Bocarsly and coworkers [16–22] have reported that PS emission can be quenched by exposure of the emitting silicon to a variety of different compounds. Among those molecules eliciting a quenching response are organic solvents, aromatic ring systems and Brönsted bases. Quenching mechanisms for porous silicon are difficult to determine, due to the heterogeneity of the system and its ill-defined photophysics. However, clear examples of energy transfer, charge transfer, and static quenching have been noted, along with other quenching phenomena which have yet to be unambiguously identified.

One relatively unique aspect of PL quenching of hydride terminated porous silicon is the large number of organic solvent quenchers which clearly can neither act as energy transfer nor charge transfer reagents. This phenomena was first reported by Sailor, who has suggested that the quenching activity is related to the dipole moment of the solvent. We have reported that this type of quenching ceases when a thin oxide layer is formed on the PS substrate (OPS). We have noted, however, that static quenching by Brönsted bases occurs even after growth of a thin oxide coating. Brönsted base quenching is only disrupted in the presence of a thick oxide surface layer. Restoration of photoluminescence from quenched samples has been reported for all classes of quenchers, but energy transfer quenchers and organic solvent quenchers usually required only that the quencher be removed from the PS environment to begin light emission, while the Brönsted bases typically required a proton source to restore emission to its initial intensity.

In order to probe the nature of Brönsted quenching, we have recently undertaken studies aimed at correlating the electron paramagnetic resonance (EPR) signal from OPS with the OPS luminescent state under quenching conditions [21]. To this end, we have employed chemically generated PS formed from polycrystalline powders. Samples of this type provided a large EPR signal. In the case of Brönsted base induced quenching an inverse correlation is observed between the PL intensity and the intensity of the EPR signal associated with interfacial dangling bonds. It had been previously determined that Brönsted base quenching is related to the abstraction of protons by the base from within the interfacial oxide layer. It is known that paramagnetic defects, called P_{b0} defects, can often be found at the silicon–silicon oxide interface. Thus it was speculated that the presence of protons in the oxide layer stabilized the diamagnetic state of potential P_{b0} sites (i.e. protons allowed two electrons to reside in such surface sites). In this model, when the nearby protons are removed, the interfacial defects revert to a P_{b0} site and localize electron–hole recombination, destroying the luminescence as shown in Fig. 1.

A typical EPR spectrum of chemically etched, chemically oxidized porous silicon powder shows two features in the EPR spectrum near $g=2$, as illustrated in Fig. 2. The signal components are assignable as follows. The lower field component of the signal has $g=2.0079$, which has been assigned to a bulk defect (referred to as K1) [23]. This paramagnetic defect is due to silicon atoms adjacent to dislocations in plastically deformed silicon. This signal is not observable by EPR in high quality single crystal silicon, but can be observed in the polycrystalline Si powders used for our EPR samples. The higher field component of the porous silicon spectrum has $g=2.0054$, close to the g-value of several features, all of which may be contributing to the signal. Polycrystalline Si, microcrystalline Si, and amorphous Si broken bond defects all have $g=2.0054\pm0.0005$, and a summation of P_b centers on many different

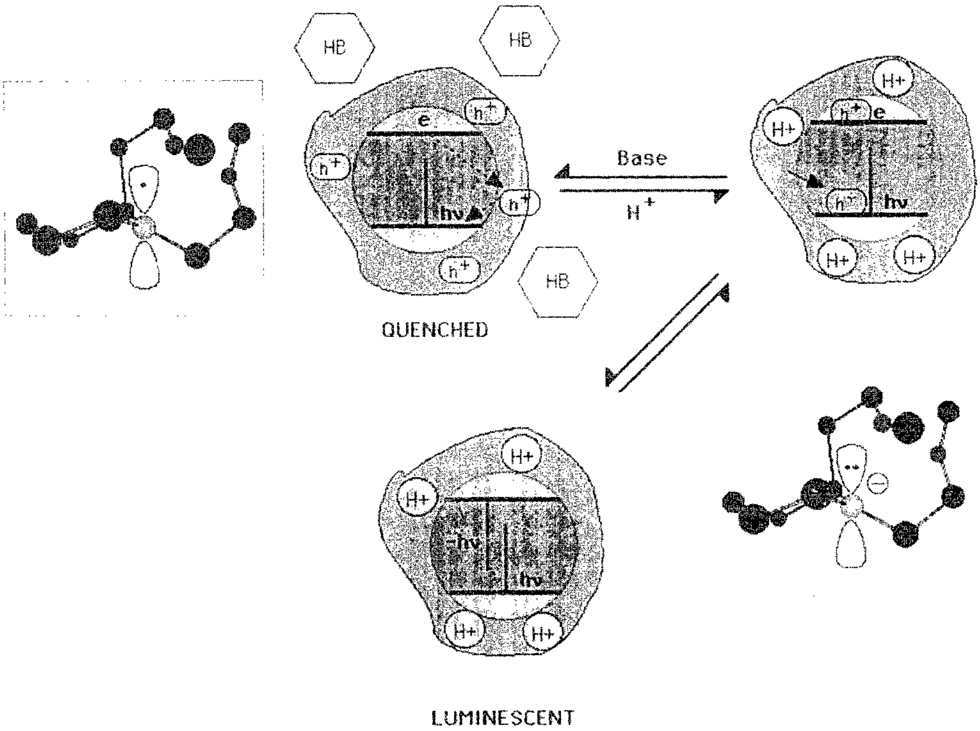

Fig. 1. Schematic diagram showing the mechanism of Brönsted base (HB) quenching of PS. Variations of the P_{b0} sites at the silicon/silicon oxide as a function of proton concentration are shown. The circular portion of the diagram represents the silicon nanoparticle, while the irregular outer portion indicates the oxide coating.

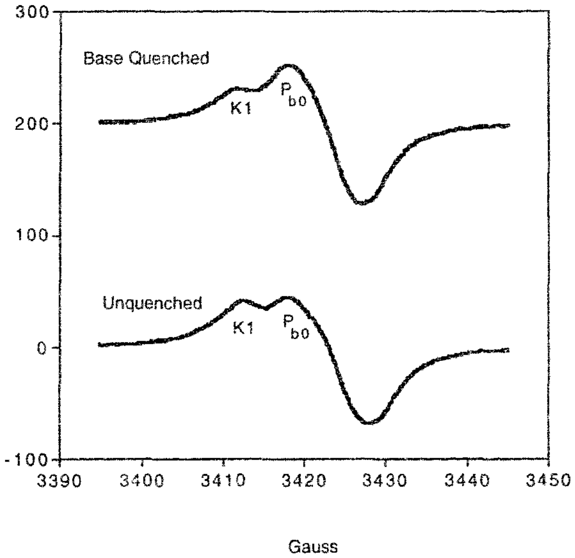

Fig. 2. EPR spectra of base quenched and unquenched oxidized porous silicon formed from a polycrystalline silicon powder. The K1 defect is a bulk defect which is invariant with quencher. The high field signal is associated with a mixture of paramagnetic species including the P_{b0} dangling bond indicated on the diagram. This signal varies with the presence of quencher. The variation is associated with the chemical interface site shown in Fig. 1.

crystalline faces has also been assigned to $g=2.005$ [24]. This latter signal is sensitive to the presence of the Brönsted base quencher, while the K1 signal is invariant and can be used as an internal standard.

When photoluminescence quenching by organic solvents and aromatics is performed using hydride terminated PS, no changes in the EPR spectrum are observed. However, once a light oxide has been formulated on the silicon, solvents and aromatics cease to have a general quenching effect, but strong photoluminescence quenching by bases is still observable. With the formation of an oxide, acidic protons become available for abstraction. The PL quenching is then accompanied by significant changes in the EPR spectrum. Hence it must be concluded that at least two different quenching mechanisms are operating, depending on the degree of surface oxidation [21].

4. Sulfur dioxide and iodine quenching

Multiple quenching mechanisms are also apparent, specifically for oxidized porous silicon. In addition to Brönsted bases, sulfur dioxide and molecular iodine are also effective quenchers of oxide coated porous silicon [20,21]. Neither quencher can be associated with a base quenching mechanism. To restore strong luminescence to SO_2 or I_2 quenched OPS, only removal of the quencher source is necessary. Partial quenching of the OPS luminescence by Brönsted bases resulted in a blue shifting of

~40 nm in the emission maximum. Similar treatment with sulfur dioxide results in a pronounced red shift of emission maximum. Plots of PL intensity versus time during exposure to SO_2 and to a Brönsted base show kinetics that are more rapid for quenching by sulfur dioxide [17]. In water, SO_2 behaves as an acid and the pH of the solution dropped to ~2. Despite the fact that an aqueous solution of pH 2 normally has a restorative effect on the PL of Brönsted quenched porous silicon due to the abundance of protons, a marked PL loss is observable when OPS is treated with SO_2 purged water. To restore PL, the sample could be removed from the aqueous solution and blown dry in air. The quenching is due to hydrated SO_2, and not to the aqueous HSO_3^- ion, as $NaHSO_{3(aq)}$ does not bring about a PL quenching response. Under these strongly acidic conditions, extraction of a surface proton by sulfur dioxide (i.e. SO_2 acting as a base) can be ruled out because of the quantity of protons in solution. Since quenching is observed, some other SO_2–surface interaction must be responsible for PL loss.

Similarly, after I_2 quenching, the emission maximum also shows blue shifts, but the only requirement for full PL restoration is removal of the I_2 source. The implication of these observations is that, like SO_2, I_2 operates by a quenching mechanism that differs from the one used to explain Brönsted base quenching of oxidized porous silicon. The fact that neither SO_2 nor I_2 requires protons for restoration hints at a stronger connection between the mechanisms responsible for SO_2 and I_2 quenching than either mechanism might have with the mechanism for base quenching.

When exposed to amines (a Brönsted base) the PL intensity of OPS is dramatically reduced, while the higher field component of the typical EPR signal grows in intensity. The lower field signal remains unchanged. If the amines are allowed to evaporate, the signal returns to its original shape and magnitude, and the PL returns to its original intensity [21]. Sulfur dioxide treatment of OPS samples also generates an EPR response. Similar to bases, the absolute number of dangling bonds on the silicon surface appears to increase in the presence of SO_2. Unlike the bases, which alter the relative magnitude of the two components, a third component grows in at a higher field than the two components already present, as shown in Fig. 3 [22]. Definite assignment of this signal to a defect is made difficult by its close proximity to the original higher field signal. For the same reason it is also difficult to determine if both original signals remain unchanged after exposure to SO_2, or if they are changing along with the appearance of the new signal. As with sulfur dioxide, iodine vapor causes a change in the EPR spectrum of porous silicon. The OPS spectrum in the presence of I_2 is similar to that observed in the presence of SO_2 in that a third component appears, separate from the two components present in the original porous silicon spectrum. For I_2, however, resolution of the third peak as a separate entity is superior, so it is more apparent by inspection that the new signal grows in without significant alterations to the shape and magnitude of the untreated porous silicon EPR spectrum.

In Fig. 3, the K1 bulk signal at $g = 2.0079$ is associated with grain boundaries. The $g = 2.0054$ signal is assigned to amorphous silicon and microcrystalline silicon bulk defects. The signal from SO_2 quenched OPS is well fit by a single Gaussian,

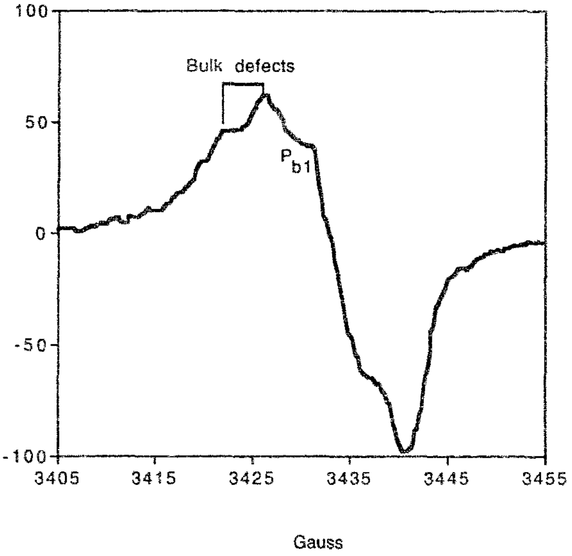

Fig. 3. EPR spectrum of OPS quenched with sulfur dioxide. The high field peak is absent in unquenched OPS spectra. This peak is associated with a P_{b1} silicon/silicon oxide surface site. The mechanism of site stabilization by sulfur dioxide is currently under investigation.

and has $g=2.0035$. There are no reported EPR signals associated with porous silicon at $g=2.0035$ to the best of our knowledge. It is known that the location of P_b defects in the EPR spectrum of amorphous silicon shifts toward lower g-value with additional O and N atoms bonded to the silicon [25]. We therefore assign the signal to an increased number of P_{b1} defects. The P_{b1} defect is similar to the P_{b0} defect, the difference being that the Si atom on which the unpaired electron resides is bonded to two silicon atoms and one oxygen atom as shown in Fig. 4.

The mechanism by which SO_2 and I_2 selectively increase the number of such sites remains unclear, but experiments thus far have yielded several important clues. First, it is apparent that neither molecule undergoes irreversible redox chemistry during its interaction with the OPS surface. After quenching with SO_2 or I_2, porous silicon restoration will occur under flowing anhydrous argon as long as the source of SO_2 or I_2 is removed, so it is unlikely that it has been oxidized or reduced. The formation of the I^- anion or the SO_4^{2-} anion on the OPS during quenching would prohibit fast restoration in air, and other reversible redox couples like SO_2/SO_2^- and I_2/I_2^- can be ruled out on thermodynamic grounds [22]. Additionally, electron transfer to iodine would result in a splitting of the EPR signal from the unpaired electron by the spin 7/2 iodine nucleus.

5. Surface modification and porous silicon sensors

The phenomenon of PL quenching lends itself to interesting sensor applications. Sulfur dioxide is a molecule of environmental concern. Since SO_2 pollution is a

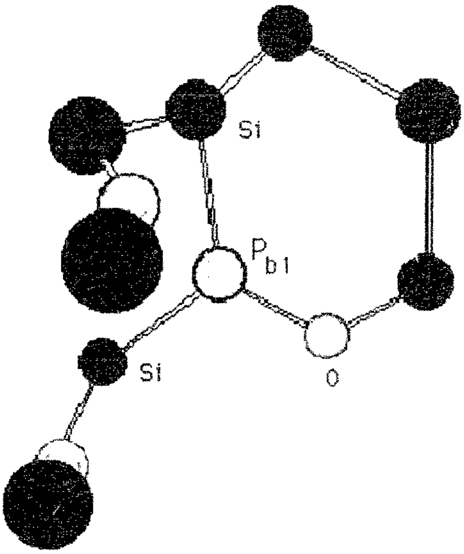

Fig. 4. Schematic of the structure of the P_{b1} site associated with sulfur dioxide induced quenching.

primary contributor to acid rain formation, its detection is important. In sulfur dioxide/argon atmospheres of greater than 10% SO_2, luminescence quenching of OPS can be clearly seen by the naked eye. Using a photodetector to detect small changes in PL intensity, the limit of detection of sulfur dioxide in argon was found to be 440 ppb [20].

There are several problems to solve before a porous silicon based SO_2 sensor could be realistically employed. At present, the surface reactivity toward sulfur dioxide lasts for several weeks. Over that period of time the layer of oxidized silicon grows thicker, and the quenching response grows weaker until eventually exposure to SO_2 results in no quenching. Preliminary experiments involving chemical modification of the OPS surface show that the SO_2 response is maintained. Since such treatments are known to inhibit the oxidation of silicon surfaces [26], it is probable that long term stabilized interfaces can be synthesized.

Chemical modification provides a route to new uses for porous silicon. Any modification that can arrest oxidation of porous silicon, either before oxide growth begins or at a desirable level of oxidation (at maximum sensitivity to sulfur dioxide quenching, for example), will prove to be useful for development of silicon based sensors. A number of approaches have been taken to modification of porous silicon surfaces. The surface has been silylated by attaching chlorosilanes to surface hydroxyls [10,17]. Water soluble polymers have been used to coat porous silicon. Organic acids have been attached to the porous silicon surface [4]. Butyl lithium has been used to attach alkyl chains to porous silicon surface. These methods have met with varying degrees of success with respect to halting oxidation.

A second potential application stemming from surface modification is the tailoring of porous silicon to sense particular molecules. It has been demonstrated that porous silicon can be modified such that water, a molecule that will not normally quench porous silicon photoluminescence, evokes a quenching response [7].

6. Conclusion

In summary, different methods of porous silicon formation lend themselves to different applications, and provide evidence for luminescence mechanisms. Multiple disruptive mechanisms are active in porous silicon photoluminescence quenching. The mechanism is affected by, among many things, the quencher and the amount of oxide on the surface. Porous silicon surfaces may also be modified to tailor them for specific uses, or to lengthen the active life span of a porous silicon sensor already suited to a particular molecule.

References

[1] L.T. Canham, Appl. Phys. Lett. 57 (1990) 1046–1048.
[2] M.T. Kelly, J.K.M. Chun, A.B. Bocarsly, Appl. Phys. Lett. 64 (1994) 1693–1695.
[3] J.C. Yee, personnal communication, 1992.
[4] M.T. Kelly, Chemistry, Princeton Press, Princeton, 1997.
[5] J.M. Lauerhaas, G.M. Credo, J.L. Heinrich, M.J. Sailor, J. Am. Chem. Soc. 114 (1992) 1911–1912.
[6] D.L. Fisher, J. Harper, M.J. Sailor, J. Am. Chem. Soc. 117 (1995) 7846–7847.
[7] J.M. Lauerhaas, M.J. Sailor, Science 261 (1993) 1567.
[8] J.L. Coffer, S.C. Lilley, R.A. Martin, L.A. Files-Sesler, Microcrystalline Semiconductors — Materials Science and Devices, Boston, MA, 1992, pp. 305–310.
[9] J.L. Coffer, S.C. Lilley, R.A. Martin, L.A. Files-Sesler, J. Appl. Phys. 74 (1993) 2094–2096.
[10] R.C. Anderson, R.S. Muller, C.W. Tobias, J. Electrochem. Soc. 140 (1993) 1393.
[11] R.C. Anderson, R.S. Muller, C.W. Tobias, Sensors and Actuators A21–A23 (1990) 835–839.
[12] J.M. Rehm, G.L. McLendon, L. Tsybeskov, P.M. Fauchet, Appl. Phys. Lett. 66 (1995) 3669.
[13] J.M. Rehm, G.L. McLendon, P.M. Fauchet, J. Am. Chem. Soc. 118 (1996) 4490–4491.
[14] G. Meyer, 1997.
[15] M.C. Ko, G.J. Meyer, Chem. Mater. 7 (1995) 12–14.
[16] J.K.M. Chun, A.B. Bocarsly, T.R. Cottrell, J.B. Benziger, J.C. Yee, Microcrystalline Semiconductors — Materials Science and Devices, Boston, MA, 1992, pp. 329–333.
[17] A.B. Bocarsly, J.K.M. Chun, M.T. Kelly, in: T.E. Mallouk, D.J. Harrison (Eds.), Interfacial Design and Chemical Sensing, vol. 561, American Chemical Society, Washington, DC 1994, pp. 78–90.
[18] J.K.M. Chun, A.B. Bocarsly, T.R. Cottrell, J.B. Benziger, J.C. Yee, J. Am. Chem. Soc. 115 (1993) 3024–3025.
[19] J.K.M. Chun, Princeton University, 1993.
[20] M.T. Kelly, J.K.M. Chun, A.B. Bocarsly, Nature 382 (1996) 214–215.
[21] M.T. Kelly, J.K.M. Chun, A.B. Bocarsly, J. Phys. Chem., in press.
[22] M.T. Kelly, A.B. Bocarsly, Chem. Mater., in press.
[23] E.R. Weber, H. Alexander, J. Phys. (Paris) 44 (1979) 101.
[24] H.J.v. Bardeleben, M. Schoisswohl, in: J. Derrien, J.-C. Vial (Eds.), Porous Silicon Science and Technology, Springer, Berlin, 1995, pp. 243–244.
[25] M.J. Powell, Properties of Amorphous Silicon, The Institute of Electrical Engineers, London, 1988.
[26] M.S. Wrighton, R.G. Austin, A.B. Bocarsly, J.M. Bolts, O. Haas, K.D. Legg, L. Nadjo, M.C. Palazzotto, J. Am. Chem. Soc. 100 (1978) 1602.